A new method using a catalytic sensor for the identification and concentration measurement of combustible gases

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Abstract : the present state-of-the-art in gas detection does not allow the precise titration of a combustible gas in air with a single catalytic sensor, because the signal depends also on other parameters than the oxidation of the gas. It is why the catalytic transducers always consist of both a detector and a compensating element. We present here a process which permits the avoidance of the compensating element, and which, moreover, allows the identification of the combustible gas and the recognition of high concentrations for some gases.

Measurement and calculation

The resistance signal on a catalytic sensor heated by the Joule effect is a combination of several processes :

$$S = S_T + S_L + S_G$$

where S_T is the signal due to the temperature of the sensor,
S_L represents thermal losses in the surroundings of the sensor,
S_G is due to oxidation of the combustible gas (in air, $S_G = O$).

On a same sensor, the catalytic oxidation of a combustible gas depends on the temperature of the sensor (see figure 1, on a platinum filament). The losses also depend - for a certain part- on this temperature. In a classical catalytic transducer, the compensating element is heated at the same temperature as the detector ; the only difference between the two signals comes from the oxidation of the gas on the detector. Here, the single sensor is heated in a discontinuous way, at several increasing temperature steps in a same sequence (see figure 2). This operation is cycled every few seconds (typically, 5 seconds or less). The **n** signals for different temperatures in clean air are memorised with the use of a micro-controller :

$$S'n = S'_Tn + S'_Ln \qquad (S'_Gn = O)$$

When a combustible gas is present in the air, the n signals become :

$$Sn = S_Tn + S_Ln + S_Gn$$

For each of the n temperatures, the measurement is calculated by the micro-controller as :

$$Sn - S'n = (S_Tn - S'_Tn) + (S_Ln - S'_Ln) + S_Gn$$

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The temperature of the filament is the same in air and (air + gas) mixture, but the thermal losses, due to a different conductivity of the combustible gas beside of air, are slightly different, so :

$$\Delta Sn = S_n - S'_n = \Delta S_L n + S_G n$$

The thermal losses depend also on the humidity and the ambient temperature, and coefficients Kn have been previously determined for the different temperatures, so that :

$$K1.\Delta S_L 1 = \Delta S_L 2$$

The measurements for the different temperatures are then compared for each couple of steps :

$$d1 = \Delta S2 - K1.\Delta S1$$

Then

$$d1 = S_G 2 - K1 S_G 1$$
$$d2 = S_G 3 - K2 S_G 2$$
$$\dots\dots\dots$$
$$d(n-1) = S_G n - K(n-1)\, S_G(n-1)$$

The identification of the gas is given by the differences d1, d2 .... The temperature steps are chosen so as, for each combustible gas to be identified, one step will be below -or just at the beginning- of the oxidation, the next step will be at the top of the response curve, for the higher oxidation of the gas. The temperature couples below the oxidation will give a null or very small signal, the couple in which the oxidation occurs will give the maximum d because $S_G m$ is high and $S_G(m-1)$ is small, the following d will be smaller because $S_G m$ and $S_G(m+1)$ have close values. The larger **d** value corresponds to a certain gas (or a family of gases for which the oxidation temperatures on the sensor are close, as for hexane and butane in our case). When the gas is identified, a coefficient is then applied to compensate the variable sensitivity of the sensor to different combustible gases. These coefficients have also been previously determined for the different gases to be measured.

Application :

We have developed an apparatus which uses this technique ; the sensor is a platinum wire of 80 µm diameter, on which the curves of figure 1 have been established. Figure 3 gives the scheme of the apparatus. We have selected 5 temperature steps, at 100°, 200°, 500°, 800°, and 1 000°C.

The temperatures are those of the warmest point of the platinum coil, e.g. the center ; the higher temperatures were measured using a micro-pyrometer, the lower temperatures (below 800°C) are calculated from the curve T = f(R), R being the resistance of the filament. With these temperature steps, we can identify :

- hydrogen,
- ethylic alcohol,
- butane,
- propane,
- methane.

The discrimination of butane from propane is deduced from the difference of their slopes between 500°C and 1000°C. For each gas to be identified, its response curve in temperature - for a fixed concentration - must first be established on the sensor.

For methane, this apparatus gives an indication when the concentration is high (over the stoechiometry) : see figure 4 the response curves for 5 selected temperatures, of methane in air, up to 100 % volume. At high concentrations (over 25 % vol/vol) the couple S_{1000} - S_{800} becomes negative, due to a greater conductivity of methane. In this case, the software gives a specific alarm.

Conclusion :

With a short pulse (less than 1 second) which consists of several temperature steps, we can, with only one catalytic sensor :

- compensate the ambient parameters,
- identify and give a good concentration of a combustible gas,
- detect for some gases, high concentrations.

The advantages are :

- a lower electrical consumption,
- a quicker response,
- a better reliability of the sensor, because the calculation compensates, to some extent, a loss of sentivity.

Some more work will be necessary to apply this technique to the identification and titration of a mixing of two, or more, combustible gases. This whole work is patent pending.

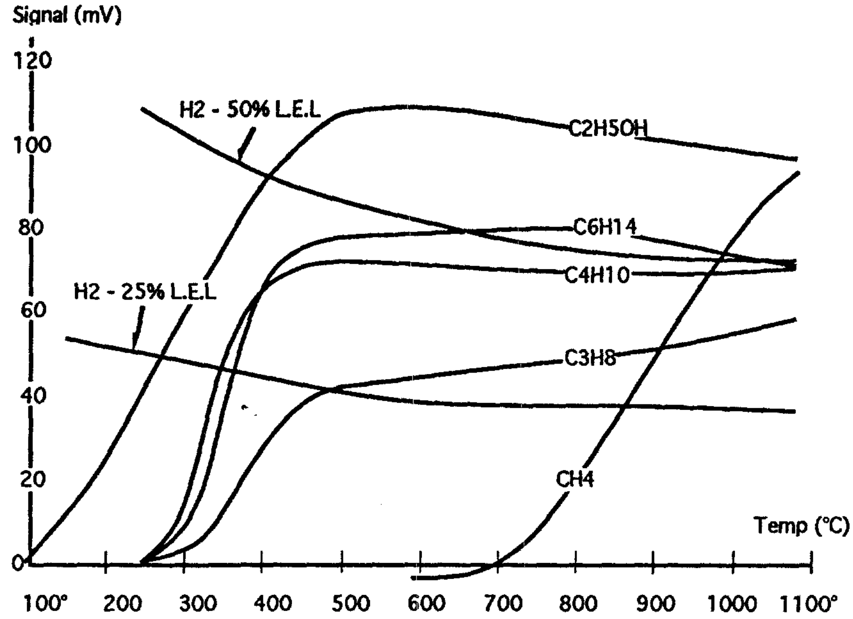

Figure 1 : response curves for several combustible gases, between 100 and 1 000°C, on a platinum filament

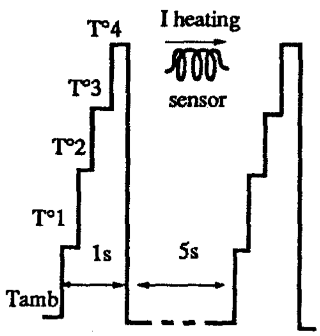

Figure 2 : heating process of the filament

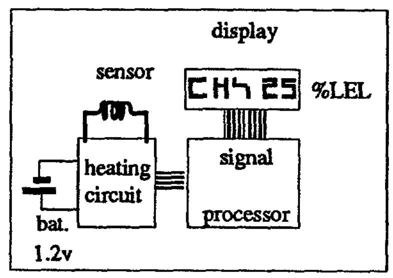

Figure 3 : scheme of the apparatus using one catalytic sensor

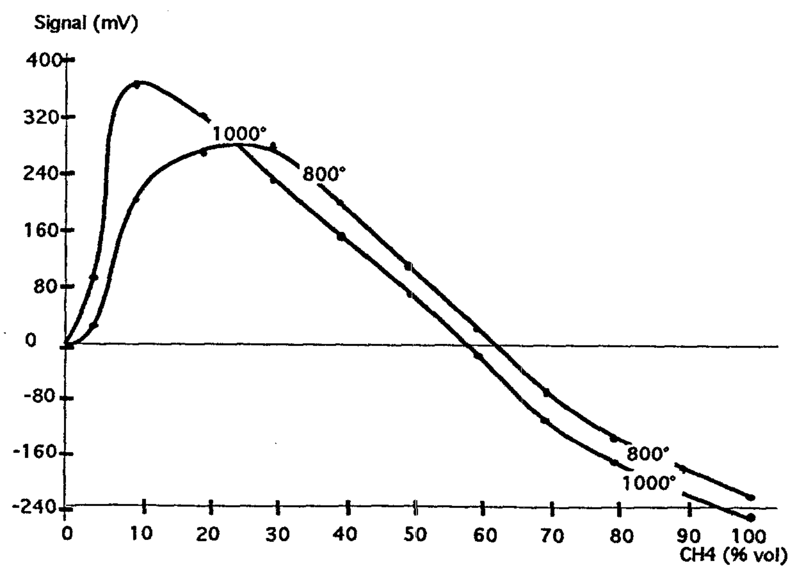

Figure 4 : response curves for methane up to 100 % vol/vol in air, at 800°C and 1000°C